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How do Buffer Layers Affect Solar Cell Performance and Solar Cell Stability?

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ABSTRACT

Buffer layers are commonly used in the optimization of thin-film solar cells. For $CuInSe_2$- and CdTe-based solar cells, multilayer transparent conductors (TCOs, e.g., ZnO or SnO_2) are generally used in conjunction with a CdS heterojunction layer. Optimum cell performance is usually found when the TCO layer in contact with the CdS is very resistive or almost insulating. In addition to affecting the open-circuit voltage of a cell, it is commonly reported that buffer layers affect stress-induced degradation and transient phenomena in CdTe- and $CuInSe_2$-based solar cells. In amorphous silicon solar cells, light-induced degradation has a recoverable and a nonrecoverable component too, and the details of the mechanism may depend on the p-type contact layer. Because of the similarity of transients and degradation in dissimilar material systems, it is suggested that degradation and recovery are driven by carriers rather than by diffusing atomic species. The question that must be addressed is why, not how, species diffuse and atomic configurations relax differently in the presence of excess carriers. In this paper, I suggest that the operating conditions of a cell can change the carrier transport properties. Often, excess carriers may enhance the conductance in localized regions ("filaments") and buffer layers; limiting current flow into such filaments may therefore control the rate and amount of degradation (or recovery).

INTRODUCTION

Those researchers skilled in they art of preparing high-performance solar cells are well aware how critical it is to get the junctions of these devices just right. It is also well acknowledged that there is no optimum recipe for the junction. Rather, the junctions have to be optimized interactively, i.e., when any one of the layers in a thin-film solar cell is altered all other layers of the cell must be "reoptimized." In the three thin-film solar cell technologies, the most critical junctions are the p/i-interface in hydrogenated amorphous silicon (a-Si:H) cells, the $ZnO/CdS/CuInSe_2$ junction in $CuInSe_2$ (CIS)-based solar cells, and in CdTe-based solar cells both the $SnO_2/CdS/CdTe$ front junction as well as the CdTe-"back-contact." Since approximately 1992, I have argued that a judicious incorporation of "inferior" (low carrier mobilty) layers near the junctions of solar cells could enhance solar cell performance by increasing the open-circuit voltage (V_{OC}). At that time, this suggestion was derived from the hypothesis that recombination processes may be transport-controlled [1]. Figure 1 shows a n/p solar cell junction with low carrier mobilities, arising from large potential fluctuation near the junction. I argued that junction recombination (V_{OC} loss as too-high mobilities – not defects - turn on j_j) could be minimized by reducing carrier mobilities or diffusivity near the junction to a minimum value required, but still allowing collection in the direction of the built-in field.

Even though prominent semiconductor physicists have proposed transport-controlled recombination processes [2 and references therein], especially for amorphous, disordered, or

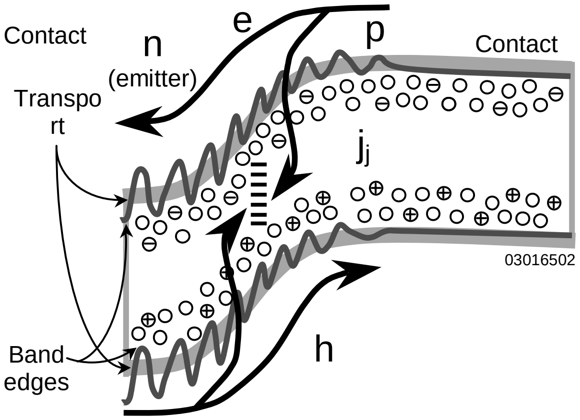

Figure 1. Schematic of solar cell n/p junction with fluctuating band edges

compensated semiconductor systems, as of now this hypothesis has not generally been accepted by the semiconductor device community as being important. Because of this apprehension, I later collaborated on using conventional solar cell device calculations to investigate the role of low mobility absorber and buffer layers. These calculations confirmed the earlier suggestions of V_{OC}-enhancement from using low-mobility buffer layers [3]. In these very fundamental and general analytical calculations, it was shown that a low mobility semiconductor absorber or buffer layer can help maximize the excess minority-carrier profile (quasi-Fermi level splitting providing an upper thermodynamic limit for V_{OC}) near the physical junction. The benefit arises because a lower diffusion length can reduce the effect of a high contact- or surface-recombination rate on the minority-carrier profile. These calculations also showed that a trade-off between V_{OC} and the short-circuit current density, J_{SC}, will occur. This is a fairly common observation in the experimental solar cell optimization process.

In CIS and CdTe solar cells, the correct buffer layer properties are realized in the resistive part of the TCO layer, the CdS layer, and in the surface of the absorber layer (low-mobility Ga/S-rich or Cu-poor surfaces in CIS and S-alloyed surfaces in CdTe cells). To prevent a reduction of V_{OC}, an enhanced resistive TCO- and/or absorber-surfaces are typically used in conjunction with thinner CdS layers. Many device processing groups reported best cell results for chemical bath deposited (CBD) CdS buffers. I suggest that the “magic” of these CBD CdS layers directly arises from their properties, namely their very fine grained and resistive nature.

Unfortunately, transient and degradation phenomena are commonly observed in many thin-film solar cells. Here, I define transients as changes that are reversible under typical operating conditions (i.e., an elastic phenomenon) and degradation as phenomena that are irreversible (i.e., inelastic) for typical operating conditions. Experimental evidence suggests a link between the phenomena. For example, exposure of a cell to moderate stress for a limited duration may cause the observed changes to be reversible. However, when the amount of stress is increased or the same stress continues for much longer duration, gradually a nonreversible degradation component is introduced. Commonly, the most important parameters for stress experiments are operating temperature and light and electrical bias applied. There is also evidence that a transient change or degradation suspected to occur in the cell absorber layers may be quantitatively altered when the same absorber is used in a cell with differently processed junctions. I suggest transport-controlled recombination in disordered semiconductors as a mechanism for transients and degradation phenomena in thin-film solar cells.

MODEL

A comprehensive model for stress-induced transients and degradation should account for general common observations:

(1) In most instances, reversible (elastic) and irreversible (inelastic) changes occur concomitantly [4,5]. In some instances, one of the components may be dominating, making the overall effect mostly elastic or mostly inelastic.
(2) Both mechanisms appear to always be affected by the presence of excess carriers.
(3) There appears to be a coupling between the elastic and inelastic effects. Sometimes, distinct memory effects are observed (the solar cell may "remember" a previous operating or stress condition) [5,6,7].
(4) Different areas of the same solar cell may show different amounts of degradation, with localized shunts forming under the worst conditions [6].
(5) Measurable chemical changes (e.g., because of a diffusing species) in the sample have to be accounted for.

Most conventional degradation models dwell on such chemical changes (item 5 from the above list) as a direct cause for degraded device performance. Most analyses focus on thermal diffusion mechanisms. The dilemma is that diffusion cannot easily account for differences in degradation with different electrical or light biases applied to the device. Therefore, sometimes combinations of ion-migration and diffusion processes are invoked. Further, degradation phenomena may be observed while a device is operated at very low temperatures (degradation at 4 K has been reported for a-Si:H cells), i.e. temperatures at which where thermally driven diffusion cannot play a role. In those instances, it is common to postulate light-induced diffusion with diffusion coefficients many orders of magnitude greater than for thermally driven diffusion.

With regard to the reversible transient phenomena, the prevailing models invoke trapping of carriers. It is experimentally well documented that the number of traps (or the occupation of existing traps) changes as the transient state of a solar cell is altered. It is therefore intriguing to postulate a certain portion (layer) in the device that would exhibit these special carrier-trapping properties. For CIS and CdTe solar cells, often the CdS junction layer has been postulated to possess the special trapping properties. However, strong transients have also been reported in ZnO/CIS cells with no CdS layer. Thus, it is unlikely that these special trapping phenomena would be associated with a specific layer or defect or trap chemistry.

In figure 2, I show on the left-hand side the conventional schematic of a "conventional" semiconductor band edge (E_C is constant, independent of location) and in the presence of potential fluctuations (E_C varies). Such a picture is occasionally accepted for polycrystalline materials based on the argument that potential barriers at the grain boundaries are the origin of the fluctuations [7]. There are well-developed similar transport theories for a-Si:H [8]. If the hypothesis of transport-controlled recombination could be accepted, the mechanism shown on the right-hand side would provide a self-consistent explanation for all transient and degradation phenomena. First, the conventional case is briefly discussed. The entrance of a new chemical or structural defect, x, can form a new defect (nd), a new trap (nt), or may form a complex or precipitate with an existing native defect (d). The latter mechanism is commonly known as defect gettering or passivation, i.e., when adding a chemical species improves the electronic quality. There is no simple explanation for elastic and inelastic changes and the observed interaction between these mechanisms from the conventional model. To make this model

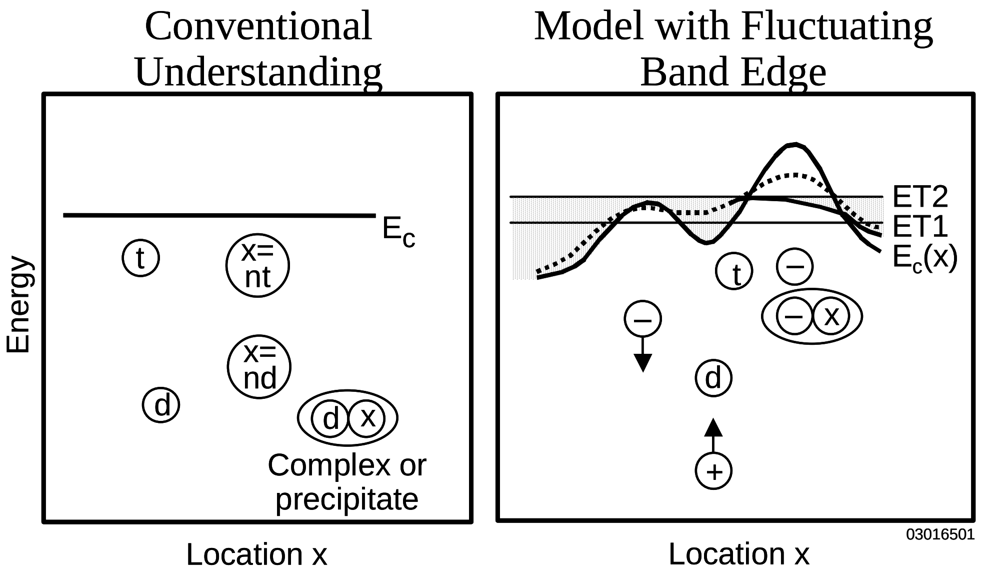

Figure. 2. Band and defect structures with and without fluctuations of the band edge

work, researchers typically postulate a complicated defect spectrum with a multitude of native and stress-induced defect levels. I suggest rejecting this approach because similar effects are observed in different materials systems or in the same material systems with different properties. For example, in CIS and CdTe cells, transients are observed in both large-grained and fine-grained cells and in devices with and without a CdS heterojunction layer.

In the case of a fluctuating band edge shown on the right-hand side of Figure 2, it is obvious that the transport in the direction of the applied field becomes dependent on the operating conditions (temperature, electric field, and carrier density optically excited or injected). As can be seen from the schematic, the transport properties will vary depending on whether a low carrier density allows transport at energy level ET1 or a greater carrier density allows transport at level ET2. It is plausible that the higher carrier densities will drive the charged defects causing the band edge fluctuations to shift, and towards relaxation if this is energetically possible. In other words, a greater carrier density will effectively reduce the magnitude of the fluctuations. If the potential fluctuations originate, as indicated, from charged defects (⊕, θ), excess carriers in the band may exert a force on these defects, causing them to shift in energy. In most material systems, eventually the underlying charged defects might relax. This mechanism is expected to be largely elastic, although a certain degree of plasticity may exist.

If an in-migrating species combines with a charged defect that acts as a source or drain for the potential fluctuations, it may permanently neutralize its charged state, which would then permanently alter the transport properties at the band edge, generally improving transport. Ultimately, I suggest that this can lead to shunting in thin film solar cells. When, because of non-uniformity, higher carrier densities (leading to greater mobility) flow in localized areas of a thin-film cell, this process is self-enhancing. In other words, a region in the absorber that begins to degrade may further enhance chemical reactions with in-diffusion chemical species, thereby causing irreversible degradation, because filaments that act as shunts are formed. Note that in this model carriers are the "driver" of the reaction of charged defects with diffusing chemical species. The proposed model explains well the formation of filaments in a-Si:H solar cells [6] and memory structures [9].

An important point is that a fluctuating band edge causes defects and traps to no longer possess a constant capture cross section. The probability that a defect will interact with a carrier in the band depends on the operating conditions (temperature, electric field, and carrier density). It is not possible to *a priori* predict a "figure of merit" for solar cell operation. The amount of charge lost to recombination with respect to the amount of charge collected may increase or decrease as changed operating conditions alter the transport properties in the fluctuating bands. Whereas better transport properties (greater effective mobilities) would imply better charge collection in a solar cell, better transport will also reduce trap occupation and generally enhance the interaction of carriers with recombination sites (increased capture rates). Only experimental experience will provide guidance as to whether cell performance increases or decreases for different device operation conditions. In some instances, a reduction of the effective carrier mobility may enhance carrier collection; an example of this is the proposed explanation by Kaydanov et al. [7] that the grain boundary in CdTe may cause enhancement of the device response. It is a common observation in CIS and CdTe solar cells that polycrystalline film solar cells outperform their single-crystal (bulk or epitaxial) counterparts. This finding is consistent with the transport model shown in figure 2. Even in the case of microcrystalline Si solar cells, best performance was reached with an "intermediate" rather than with the largest grain structure [10]. It is crucial that the thin-film solar cell community questions the traditional "more perfection equals improvement" thinking.

MODEL PREDICTIONS

In thin-film solar cells, appropriate buffer layers that are required to obtain high V_{OC}-values may, because of their resistive nature, limit the amount of current that can rush into a small localized area and drive a filament or shunt formation process. Assuming that the degradation processes are driven by carrier flow, this can explain why using the same cell absorber in a device with different buffer or junction layers can lead to observed differences in the amount and kinetics of the degradation phenomena. There is considerable concern about cells with very thin (for CIS and CdTe, <1-µm-thick) absorber layers. Often such cells have lower values of V_{OC} and appear shunted. It is normally suggested that absorbers which are too thin would be prone to physical damage, e.g., from diffusing species, and susceptible to unavoidable shunt formation. I suggest that in many instances, insufficient buffering or absorber layers with carrier mobilities that are too high for the respective absorber thickness may become the cause not only for low V_{OC} value [11], but also of the apparent shunting. Thus, as long as the degradation is driven by carriers, thinner absorber layer cells should be as stable as thicker ones once they are optimized and attain the same V_{OC} values as thick cells. It is interesting to note that this has clearly been realized in the case of a-Si:H solar cells. For this material, extremely thin cells (absorber thicknesses of about 200 nm) have achieved high V_{OC} and actually exhibit the least amount of light-induced degradation, and shunting is not a problem even when optically enhancing rough substrates are used. In summary, acceptance of my proposed model would suggest the following:

(1) Thinner cells that requiring more "buffering" and perhaps lower mobility absorbers in order to achieve high V_{OC} values may be as stable as thicker cells.

(2) Manipulating the concentration of the “diffusing culprit” (H in a-Si, Cu in CdTe) will not be effective to minimize or eliminate cell transients and degradation.

(3) High-V_{OC} cells should degrade the least relative amount. This is true as long as stress induced changes in the buffer layer themselves do not lead to V_{OC} loss. If V_{OC} loss is observed, more stable junction or buffer recipes have to be employed, or the absorber diffusion length has to be further **reduced** short of the point at which carrier collection becomes impossible.

(4) If diffusion “follows” rather than “leads” the electronic changes, we will not understand stress-induced changes from detailed structural and chemical analyses and diffusion studies. We will study a correlation, not a cause and effect relationship.

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